

NATURAL VARIABILITY OF MINOR AND TRACE ELEMENTS IN TWO SPECIES OF  
WESTERN PACIFIC SCLEROSPONGES

Research Thesis

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Dana Borg

The Ohio State University

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Approved By

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Dr. Andréa G. Grottoli  
School of Earth Sciences

## Abstract

Elemental proxies are used to reconstruct oceanic conditions that pre-date modern records. Such proxies have been established in corals, but few attempts have been made in sclerosponges. *Acanthocheatetes wellsi* (high Mg-calcite, collected from Palau and Saipan) and *Astrosclera willeyana* (aragonite, collected in Saipan) were stained in situ and left to grow on the reef for two years. We measured P, Pb, Sr and Ba (standardized to Ca) in two-year bulk samples from all specimens and 0.5mm high-resolution samples from two *A. wellsi* from Palau, one *A. wellsi* and one *A. willeyana* from Saipan. Interspecific differences in bulk P/Ca, Pb/Ca, Sr/Ca, and Ba/Ca are likely due to mineralogical effects. Bulk sclerosponge P/Ca was higher, and Pb/Ca was lower, in Palau than in Saipan suggesting that these elements are sensitive to regional oceanographic conditions. At high-resolution, only P/Ca signatures were highly reproducible within and among species indicating that sclerosponges reliably record these elemental ratios in their skeletons. Furthermore, the apparent relationship between P/Ca, temperature, rainfall, and nutrient concentrations in Saipan indicates that sclerosponge P/Ca could be a paleonutrient recorder.

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## 1. Introduction

Sclerosponges are slow-growing reef organisms that deposit their calcium carbonate skeleton in sequential layers over time. They are found throughout the tropics across a 1000 m depth range and can live for hundreds of years (BOHM et al., 1996; DRUFFEL and BENAVIDES, 1986). The isotopic and elemental compositions of sclerosponge skeletons are increasingly used to reconstruct tropical paleoceanographic records. The ratio of stable oxygen isotopes ( $\delta^{18}\text{O}$ ) in sclerosponge skeletons appears to track the  $\delta^{18}\text{O}$  composition of seawater and is thus used primarily as a seawater temperature proxy (GROTTOLI et al., 2010; MOORE et al., 2000). Phosphorus (P), lead (Pb), and barium (Ba) are potential proxy recorders of upwelling due to the difference in their concentration in surface waters versus deep water (LAVIGNE et al., 2008; MATTHEWS et al., 2008; SWART et al., 2002) that once calibrated, could enhance the information obtained from sclerosponge records. During upwelling events, cold, nutrient rich waters are drawn to the surface resulting in increases in skeletal P/Ca and Ba/Ca, and decreases in Pb/Ca (LAVIGNE et al., 2008; MATTHEWS, 2007; MATTHEWS et al., 2008). In addition, Sr/Ca in sclerosponge skeletons appears to reliably record temperature variations with a negative correlation to temperature in the Caribbean sclerosponge *Ceratoporella nicholsoni* (HAASE-SCHRAMM et al., 2003; ROSENHEIM et al., 2004; SWART et al., 2002) but not the Pacific species *Astrosclera willeyana* (FALLON et al., 2005; GROTTOLI et al., 2010). However, the elemental ratios P/Ca and Ba/Ca have not been measured in any sclerosponges to date, Pb/Ca has not been measured in any Pacific sclerosponges, and Sr/Ca has not been measured at high-resolution in *Astrosclera willeyana*. Thus, elemental ratios in sclerosponges offer a large untapped source of potential paleo proxy recorders.

*A. wellsi* has a high-Mg calcite skeleton (21mol%) (GROTTOLI et al., 2010) at a density of 1 g/cm<sup>3</sup> (Grottoli, unpublished) and deposits its skeleton in distinct layers with little to no secondary infilling. In contrast, both *A. willeyana* and *C. nicholsoni*, the other two main species used for paleo-reconstructions, have aragonitic skeletons with densities near that of pure calcite (2.7 g/cm<sup>3</sup>) (FALLON and GUILDERSON, 2005), do not have visible layers, and have significant secondary infilling of the skeleton (WILLENZ and HARTMAN, 1989; WORHEIDE et al., 1997). Such variations in skeletal structure and mineralogy could have significant effects on the elemental proxy records generated from these organisms, which could significantly influence our ability to compare proxy records generated from multiple specimens or species.

Here, the variations in P/Ca, Sr/Ca, Ba/Ca, and Pb/Ca, were examined in multiple specimens of *A. wellsi* and *A. willeyana* sclerosponges grown in situ at the Short Drop Off Reef in Palau and at The Grotto in Saipan for 2 years. With these specimens, the following hypotheses were tested: (1) P/Ca, Pb/Ca, Sr/Ca, and Ba/Ca significantly differ between locations (Palau versus Saipan and species (*A. wellsi* versus *A. willeyana*)) and (2) the concentrations of these elements change with time and are sensitive to oceanic conditions.

## **2. Methods**

### **2.1. Field Site**

Palau is located in the northwestern quadrant of the western Pacific warm pool (WPWP). Short Drop Off, Palau (7°16' N, 134°31' E) is a reef wall located 2 km offshore (Figure 1). Short Drop Off has a local current that travels the length of the wall, is not influenced by runoff from land or temperature and salinity dynamics of caves or lagoons. The *A. wellsi* sclerosponges used in this study were within 1 m of large crack/crevice openings and were found at depths ranging from 5 to 20 m.

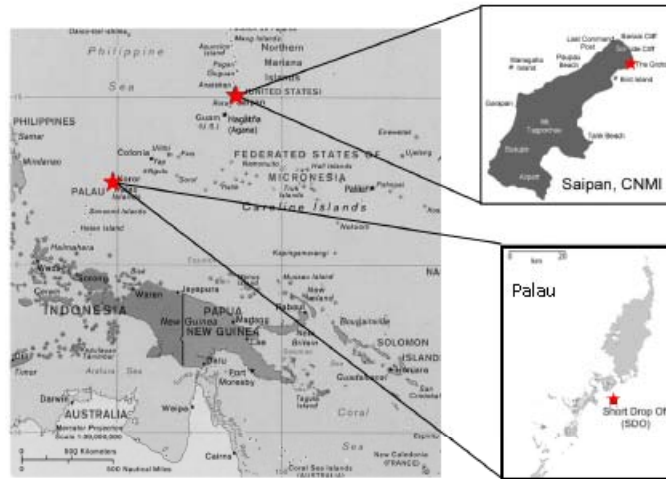


Figure 1. Map of field sites.

Saipan is located 1,500 km to the northeast of Palau in the Central Northern Mariana Islands chain and is outside of the WPWP. The Grotto, Saipan ( $15^{\circ}2' \text{ N}$ ,  $145^{\circ}6' \text{ E}$ ), is a large swim-through cavern located on the northeastern tip of the island (Figure 1). The Grotto is flushed by the predominant North Equatorial Current waters that flow past the site, is not influenced by temperature and salinity dynamics of closed caves or lagoons, and is minimally affected by runoff from land. Both *A. wellsi* and *A. willeyana* sclerosponges grow here between 6 and 33 m depths along the walls of the cavern.

## 2.2. Two Year Calibration Experiment

A complete description of the collection methods is available in Grottoli et al. (2010). In brief, seven *A. wellsi* sclerosponges were identified between 11.5 and 18 m depths along the wall at Short Drop Off, Palau. The specimens were stained with Alizarin Red on 26 July 2001, re-cemented onto the reef at 11 m depth using Splash Zone® marine epoxy, and allowed to grow

out past the stain line for 2 years. In Saipan, three *A. wellsi* were identified at 6 m depth and four *A. willeyana* sclerosponges were identified between 7 and 9 m depth, were also stained with Alizarin Red on 15 July 2001, re-cemented onto the reef at 8.3 m depth with marine epoxy, and allowed to grow out past the stain line for 2 years (Figure 3). On 15 July 2003 all of the specimens were collected from Palau, and 11 July 2003 from Saipan, and were returned to the lab for further analysis. Due to the lack of reliable annual skeletal banding (Figure 3E, F), the staining all of the specimens on a known date ensured that a clearly identifiable common time period was present in each specimen, allowing them to be sampled and compared over the exact same time period. In addition, by allowing the specimens to grow in situ at equal depths within each location ensured that the sclerosponges grew under common natural conditions, thus removing any possible depth effects on the interpretation of the results.

Once in the laboratory, each specimen was cut down its major growth axis, cleaned with deionized water, and dried at 60°C for 3 days. The sclerosponges were then sampled in two ways. First, bulk measurements spanning the entire 2 year common time period that was established with the stain lines were obtained from each specimen. Each bulk skeletal sample was milled from the stain line to the growing edge using a Dremmel tool fitted with a diamond-tipped dental drill bit.

Second, high-resolution samples were collected by two *A. wellsi* specimens from Palau, one *A. wellsi* specimens from Saipan, and one *A. willeyana* specimens from Saipan at 0.5 mm increments with a Merchantek Micromill from the growing edge to the stain line.

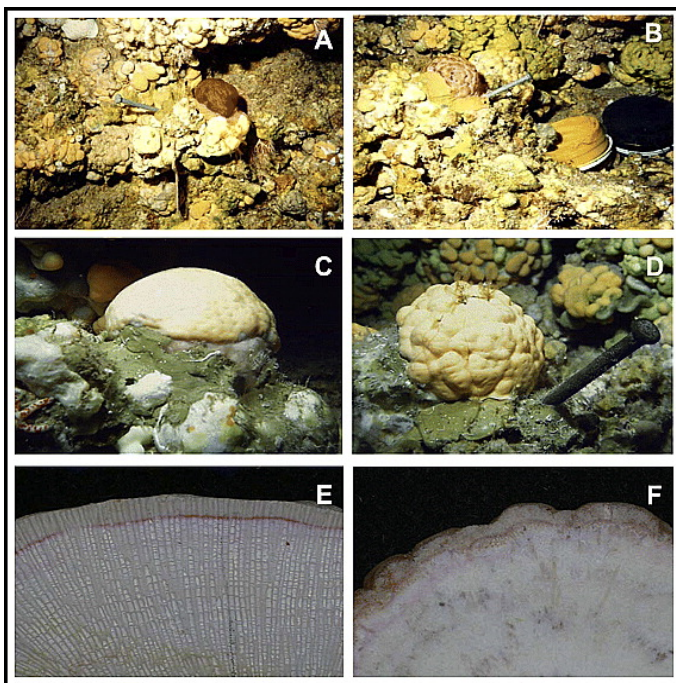


Figure 2

Sclerosponges *Acanthocheatetes wellsi* (left), *Astrosclera willeyana* (right) in situ and in cross section. (A, B) Sclerosponges in situ immediately after staining, (C, D) 1 year after staining, and (E, F) in cross section, showing full two years of growth. Note the clear vertical and horizontal skeletal features with little backfilling in E and the absence of clear skeletal features and heavy backfilling F. Photos by J.M. and A.G.G..

### 2.3. Sample Solutions and Standards

All solutions were made with MilliQ water (18 mΩ; Millipore, MA) and ultrapure reagents unless otherwise noted. All labware was pre-cleaned with 5% HNO<sub>3</sub>, 20% HCl and MilliQ for a minimum of 10 hours each prior to sample handling in a Laminar Flow Hood.

Gravimetric standards were used to make calibrations curves for P, Pb, Sr, Ba, and Ca. Stock standard solutions (CPI International) were diluted with ultrapure 2% HNO<sub>3</sub> to concentrations that matched expected sample concentrations.



## 2.4. Sample Preparation

Bulk sclerosponge samples of approximately 10mg were pre-cleaned for elemental analysis following methods described in Matthews et al. (2006). In brief, samples were ultrasonicated in MilliQ water, oxidized in a solution of 50:50 0.2M NaOH and 30% H<sub>2</sub>O<sub>2</sub>, reduced using hydrazine buffered in 50:50 mixture of 30% NH<sub>4</sub>OH and 0.25M (NH<sub>4</sub>)<sub>2</sub>C<sub>6</sub>H<sub>6</sub>O<sub>7</sub>, and leached in 0.001M HNO<sub>3</sub>, with sub-boiling heat baths and ultrasonication, and multiple MilliQ water rinses between each step. Following cleaning, samples were dissolved in 6mL of 2% HNO<sub>3</sub>. High-resolution 0.5 mg samples were prepared in the same method with the exception that they were dissolved into 2.5mL of 2% HNO<sub>3</sub>.

## 2.5. Elemental Analyses

Measurements were carried out on a Finnigan Element 2 Inductively Coupled Plasma-Sector Field Mass Spectrometer (ICP-SFMS) using low resolution (with the exception of P and Sr at medium resolution) and operated in E-scan mode. Internal standards of Co, Rh, and Bi were used to correct for signal drift over the course of the run, blank corrected, and then concentrations calculated using the calibration curves from the gravimetric standards. For quantification, <sup>43</sup>Ca, <sup>31</sup>P, <sup>208</sup>Pb, <sup>86</sup>Sr, and <sup>138</sup>Ba were used. At least one additional isotope of each element was monitored to check for interferences. P, Pb, Sr, and Ba concentrations were standardized to Ca content.

## 2.6. Data Analysis

Significant differences in bulk P/Ca, Pb/Ca, Sr/Ca, and Ba/Ca between *A. wellsi* at Palau and Saipan (location effect), and between *A. wellsi* and *A. willeyana* species in Saipan (species effect), were each tested by one-way analysis of variance (ANOVA), where effects were statistically significant at  $p < 0.05$ . Direct comparison between locations could be

done only with *A. wellsi* since *A. willeyana* was not present at both sites. A direct comparison between species could only be done at Saipan, where both species occurred. High- resolution data was visually assessed and qualitative comparisons made.

### **3. Results**

#### **3.1. Bulk Data**

Average bulk sclerosponge P/Ca was significantly higher (Figure 3A) ( $F=6.34$ ,  $p=0.0399$ ,  $df=8$ ) and average bulk Pb/Ca was significantly lower (Figure 3B) ( $F=100.65$ ,  $p<0.0001$ ,  $df=8$ ) in *A. wellsi* from Palau than in *A. wellsi* from Saipan. Bulk average *A. wellsi* Sr/Ca and Ba/Ca did not differ significantly between locations (Figures 3C, D) ( $F=0.31$ ,  $p=0.5962$ ,  $df=8$ ;  $F=1.11$ ,  $p=0.3265$ ,  $df=8$ , respectively).

Within the Saipan site, the average bulk sclerosponge P/Ca and Pb/Ca were significantly higher (Figures 3E, F) ( $F=148.36$ ,  $p<0.0001$ ,  $df=6$  and  $F=68.88$ ,  $p=0.0004$ ,  $df=6$ , respectively) in *A. wellsi* than in *A. willeyana*. Sr/Ca was significantly lower in *A. wellsi* than in *A. willeyana* in Saipan (Figure 3G) ( $F=111.56$ ,  $p<0.0001$ ,  $df=6$ ). Bulk Ba/Ca did not significantly differ between the two species (Figure 3H) ( $F=0.49$ ,  $p=0.5236$ ,  $df=6$ ).

#### **3.2. High-Resolution Data**

The 2-year high-resolution P/Ca (Figure 4A) and Sr/Ca (Figure 4C) records were reproducible while the Pb/Ca (Figure 4B) and Ba/Ca (Figure 4D) records were not reproducible between the two Palauan *A. wellsi* specimens. The interannual P/Ca records of *A. wellsi* and *A. willeyana* from Saipan, though offset between the two species, were very reproducible (Figure 4E). The interannual Pb/Ca, Sr/Ca, and Ba/Ca records were very dissimilar (Figure 4F, G, and H).

The general patterns seen in the bulk analyses were similar when comparing the averages in the high-resolution data. *Acanthocheatetes wellsi* in Palau had higher P/Ca and lower Pb/Ca than in Saipan. In Saipan, *A. wellsi* had higher P/Ca and Pb/Ca than *A. willeyana*, while Sr/Ca was lower.

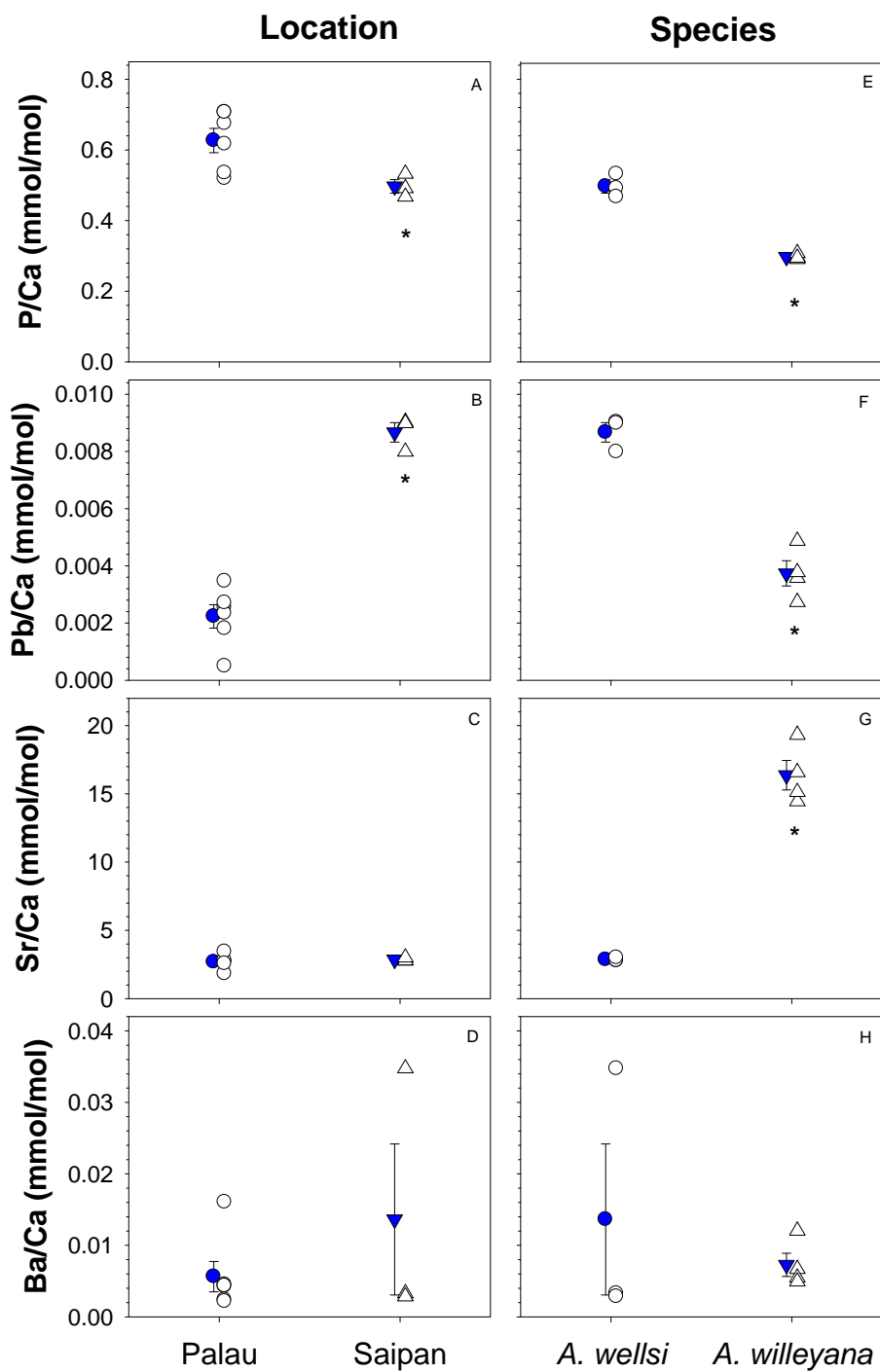


Figure 3: Bulk Data. (A-D) Location (Palau *A. wellsi* vs Saipan *A. wellsi*) and (E-H) Species (Saipan *A. wellsi* vs Saipan *A. willeyana*) variation in two-year bulk Ba/Ca, Pb/Ca, P/Ca, and Sr./Ca. Open symbols represent individual sample values, closed symbols are averages  $\pm 1$  standard error. \* =  $p < 0.05$

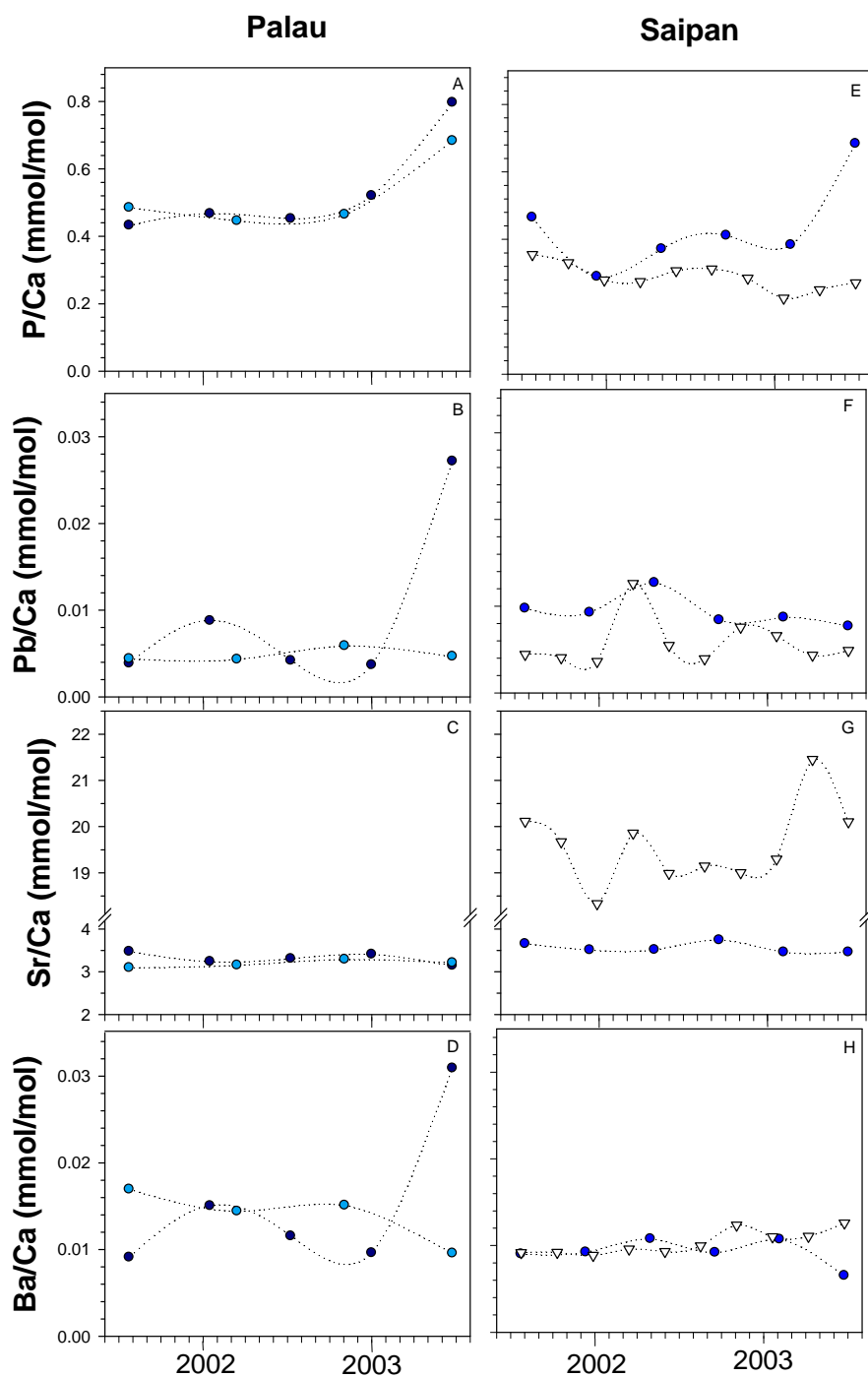


Figure 4: High-Resolution P/Ca, Pb/Ca, Sr/Ca, and Ba/Ca. (A-D) Palau [*A. wellsi*; two specimens] and (E-H) Saipan [*A. wellsi* (circles) and *A. willeyana* (triangles) variation in 0.5mm increments].

## 4. Discussion

### 4.1 Phosphorus

Elevated bulk P/Ca in Palauan *A. wellsi* than in Saipan (Figure 3A) is most likely due to upwelling at that site as phosphorus is more abundant in the nutrient rich, deep waters (WILLIAMS and GROTTOLO, 2010; YANG and WANG, 2009). Within Saipan, the difference in average bulk P/Ca between *A. wellsi* and *A. willeyana* could be due to the different mineralogies (high Mg-calcite vs aragonite), differences in their skeletal structure (no backfilling vs backfilling), or some species-specific metabolic effect (Figures 2E, F). High-resolution P/Ca records were consistent between specimens at both locations. In Palau sclerosponge P/Ca increased dramatically during the last six months of the record (Figure 4A), corresponding to a shoaling of the nutricline and the depletion of seawater  $\delta^{18}\text{O}$  in the region (GROTTOLO et al., 2010; WILLIAMS and GROTTOLO, 2010). Nutricline shoaling in Palau fluctuates both seasonally and on El Niño-Southern Oscillation (ENSO) timescales and is characterized by the presence of higher nutrient levels in the mixed layer (COLIN, 2001; WILLIAMS and GROTTOLO, 2010; ZHANG et al., 2007). Seawater  $\delta^{18}\text{O}$  in the region also varies on seasonal and ENSO timescales as a result of water mass mixing (GROTTOLO et al., 2010). Thus, sclerosponge P/Ca appears to record changes in nutrient levels associated with nutricline fluctuations. In Saipan, the P/Ca ratio increased during the summer rainy months and decreased during the drier winter months (Figure 4E, 5). As these sclerosponges are located in a large carbonate swim-through cave, increases in rainwater percolation and transport of nutrients from the overlying soil and vegetation, could be the underlying driver of seasonal variation in P/Ca detected in the Saipan sclerosponges. In situ measurements of seawater P concentrations over the course of a year at both Palau and Saipan are needed to fully validate the relationship between seawater P and sclerosponge P/Ca.

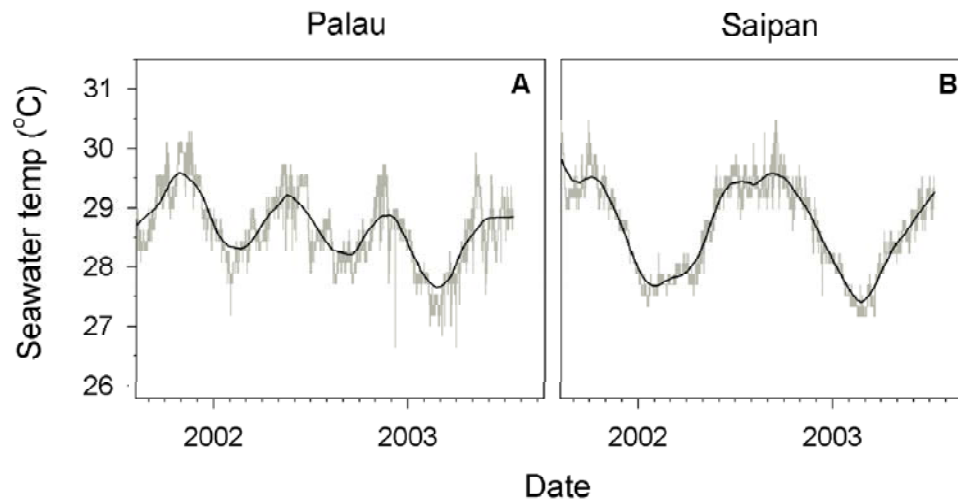


Figure 5. Hourly seawater temperature (a) in Palau and (b) in Saipan. Measurements were recorded from July 2001 to July 2003. Individual measurement values are plotted in gray. Smoothed trendline is plotted as black solid line.

## 4.2 Lead

Lower bulk Pb/Ca Palauan *A. wellsi* than in Saipan, is most likely due to upwelling as well (Figure 3B). Surface waters have higher concentration of Pb due to the anthropogenic burning of fossil fuels (LAZARETH et al., 2000; ROSENHEIM et al., 2005; SWART et al., 2002). During upwelling, Pb depleted deeper waters are entrained to the surface diluting surface concentrations and driving the Pb/Ca values in sclerospores down. In addition, bulk Pb/Ca was higher in *A. wellsi* compared to *A. willeyana* in Saipan (Figure 3F). This is also most likely due to the mineralogical, structural, or metabolic differences between the species (Figures 2E, F). However, the Pb/Ca ratios in both species are three orders of magnitude higher than previously reported in the aragonitic Caribbean sclerosponge *Ceratoporella nicholsoni* that was collected at 143 m (ROSENHEIM et al., 2005). This is not unexpected as Pb penetration from the surface would be much lower at these depths. However, despite the depleted bulk Pb/Ca values in Palau, inconsistencies in high resolution Pb/Ca between the two *A. wellsi* specimens in Palau (Figure

4B) and between both species in Saipan (Figure 4F) indicates this element is not suitable for tracking the timing of upwelling events.

### 4.3 Strontium

Several studies have shown Sr/Ca in sclerosponge skeletons to reliably record temperature variations of seawater (HAASE-SCHRAMM et al., 2003; ROSENHEIM et al., 2004; SWART et al., 2002). In this study, average bulk *A. wellsi* Sr/Ca did not differ between sites (Figure 3C) and is supported by the similarity of their two-year average temperatures (Palau  $28.66^{\circ}\text{C} \pm 0.62$ , Saipan  $28.70^{\circ}\text{C} \pm 0.79$ ; Figure 5) (GROTTOLI et al., 2010). In Saipan, lower bulk Sr/Ca in *A. wellsi* compared to *A. willeyana* (Figure 3G) is likely due to mineralogical differences between the species where the Mg in the high-Mg calcite skeleton of *A. wellsi* interferes with the incorporation of Sr into the skeleton (GROTTOLI et al., 2010; MORSE and BENDER, 1990). High-resolution Sr/Ca in Palau is consistent between specimens (Figure 4C) but does not capture the biannual temperature signal in Palau due to the low sampling resolution and/or because *A. wellsi* Sr/Ca records are insensitive to temperature. In Saipan, Sr/Ca records do not agree well between the two species. This is likely due to the smoothing effect that is created by the backfilling of the *A. willeyana* skeleton where approximately 1/3 of the skeletal material is initially deposited and the remaining 2/3 is filled later (FALLON et al., 2005). Analyzing additional specimens of *A. wellsi* from Saipan are needed to determine the full potential of sclerosponge Sr/Ca as a reliable recorder of seawater temperature.

### 4.4 Barium

There were no significant differences in Ba/Ca both between species and locations (Figures 3D, H) suggesting that this element is insensitive to oceanographic conditions in these



species in the western tropical Pacific. This is reflected in the inconsistencies in the high-resolution data in between specimens in Palau and between species in Saipan (Figures 4D, H).

#### **4.5 Summary and Recommendations for Future Work**

Based upon the bulk data, P/Ca and Pb/Ca show the most promise as upwelling proxy recorders on biannual or longer timescales. However, high-resolution analyses indicate that only P/Ca has potential to be used as a high-resolution paleonutrient recorder. Laser ablation and higher resolution in situ seawater measurements are needed to fully calibrate P/Ca as a proxy recorder of upwelling and/or nutrients. In addition, further study of *A. wellsi* sclerosponges is needed to determine if Sr/Ca may be useful as a temperature recorder.

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